

**COMPOSITE CARBON FIBER REINFORCED OF A NEW
AMORPHOUS, ASYMMETRIC, ADDITION TYPE
POLYIMIDE (TRIPLE A - PI)**

Rikio Yokota

Institute of Space and Astronautical Science (ISAS)
3-1-1 Yoshinodai, Sagamihara-shi, Kanagawa, 229-8510, Japan

Toshio Ogasawara

National Aerospace Laboratory of Japan (NAL)
6-13-1, Osawa, Mitaka-shi, Tokyo, 181-0015, JAPAN
TEL 0422-40-3561, FAX 0422-40-3549, E-mail ogasat@nal.go.jp

Hideki Ozawa, Mitsushi Taguchi, and Ryouichi Sato
Ube Industries, Ltd.

8-1, Goi-minamikaigan, Ichihara-shi, Chiba, 290-0045, Japan

Yu Shigenari and Kiyoshi Miyagawa

IHI Aerospace Co., Ltd.
900, Fujiki, Tomioka-shi, Gunma, 370-2398, Japan

ABSTRACT

This paper presents experimental results for the processing and mechanical properties of carbon fiber reinforced composites with a newly developed amorphous, asymmetric, and addition type polyimide (Triple A-PI). The imide oligomers were synthesized from the reaction of 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), 4,4'-oxydiaminine (ODA), and phenylethynyl phthalic anhydride (PEPA). Because of amorphous structure, the melting point and melt viscosities of the polymer are relatively lower as compared with similar polyimides such as LaRC™ PETI-5. In spite of the lower molecular weight of the imide oligomer (<5000 g/mole), the cured polymer exhibits excellent mechanical properties because of the irregular and asymmetric structure as well as flexible end-capper. Carbon fiber reinforced composites were fabricated by routing prepreg consolidation. The composites exhibit excellent mechanical properties with high glass transition temperature (>300°C).

KEW WORDS: Polyimides, High Temperature Composite, Mechanical Properties

1. INTRODUCTION

Polyimides are attractive for aerospace applications because of their excellent thermo-oxidative stability and mechanical properties. The processability of polyimides is inferior as compared with epoxies and bismaleimides. Phenylethynyl terminated polyimide LaRC™ PETI-5 developed by NASA Langley Research Center (LaRC) possesses good processability and excellent mechanical properties for an adhesive and composite matrix resin [1-4]. Therefore, a great amount of effort has been devoted to application of PETI-5 to the Mach 2.4 high-speed civil transport (HSCT) project in the United States for several years [5].

For PETI-5, random co-oligomer prepared from 3,3',4,4'-BPDA (3,3',4,4'-Bipheyltetracarboxylic dianhydride, s-BPDA), 3,4'-ODA (oxydiamiline), 1,3-APB (bis 3-aminophenoxy benzene), and 4-PEPA (Phenyl- ethynylphthalic anhydride) has been applied in order to decrease melt viscosities.

Recently, a new addition type polyimide was developed from the reaction of 2,3,3',4'-BPDA(a-BPDA), diamine, and PEPA under the collaboration between the Institute of Space and Astronautical Science (ISAS) and Ube Industries Ltd. In Japan[6-8]. A new polyimide is referred to as "Triple A-PI (TA-PI)" from the characteristics of the polymer (amorphous, asymmetric, and addition type), and this is provided by Ube Industries Ltd. (commercial name, UPILEX™-AD). Both the imide oligomers and cured polymers have significantly irregular and asymmetric structure derived from asymmetric (a-)BPDA, resulting in low melting point and melt viscosities. Furthermore, even though the molecular weight of the imide oligomer is relatively low, the cured polymer exhibits excellent mechanical properties, with high glass transition temperature ($T_g > 300^\circ\text{C}$) [9-10].

Higher heat resistance will be necessary for future reusable launch vehicles and jet engine applications as well as HSCT. National Aerospace Laboratory of Japan, Institute of Space and Astronautical Science, Ube Industries Ltd., and IHI Aerospace Co. Ltd. have conducted a joint program to develop and evaluate the composite system since September 1999 [10]. Lower molecular weight Triple-A PI polymers were selected for higher glass transition temperature ($T_g > 300^\circ\text{C}$), and lower melt viscosities without affecting the mechanical properties (toughness and elongation). This paper presents preliminary experimental results for processing and mechanical properties of carbon fiber reinforced composites with the 1600 and 2600 g/mole version imide oligomers. The effects of imide oligomer molecular weight and cure temperature on the composite properties were also investigated.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of Triple A-PI

2.1.1 Synthesis of polyamide acid and imide oligomers

The synthetic scheme for the imide oligomer is shown in Fig. 1. The diamine (4,4'-ODA) was initially dissolved in NMP at room temperature under nitrogen. The dianhydride (a-BPDA) and endcapper (PEPA) were added in the 4,4'-ODA / NMP solution, and the reactions were allowed to stir for 3 hrs at room temperature under nitrogen. The amide acid / NMP solutions were used for preparation of prepreg tapes and prepreg fabrics. The imide oligomers with different molecular weight (calc. ~ 1600 ($n=2$), ~ 2500 ($n=4$), and ~ 5250 g/mol ($n=10$)) were synthesized through the amide acid route in NMP.

Table 1 Physical Properties of Imide Oligomers

	$n=2$	$n=4$	$n=10$
Molecular weight (calc.), Mn	~ 1600	~ 2500	~ 5250
Imide oligomer T_g ($^\circ\text{C}$) *	189	230	237
Imide oligomer minimum melt viscosity (Pa sec)	3.4 (336°C)	124 (347°C)	1750 (369°C)
Cured polymer T_g ($^\circ\text{C}$) * **	351	341	308

* Determined on powdered samples by DSC at a heating rate of $10^\circ\text{C}/\text{min}$.

** Cured at 370°C for 1 hr.

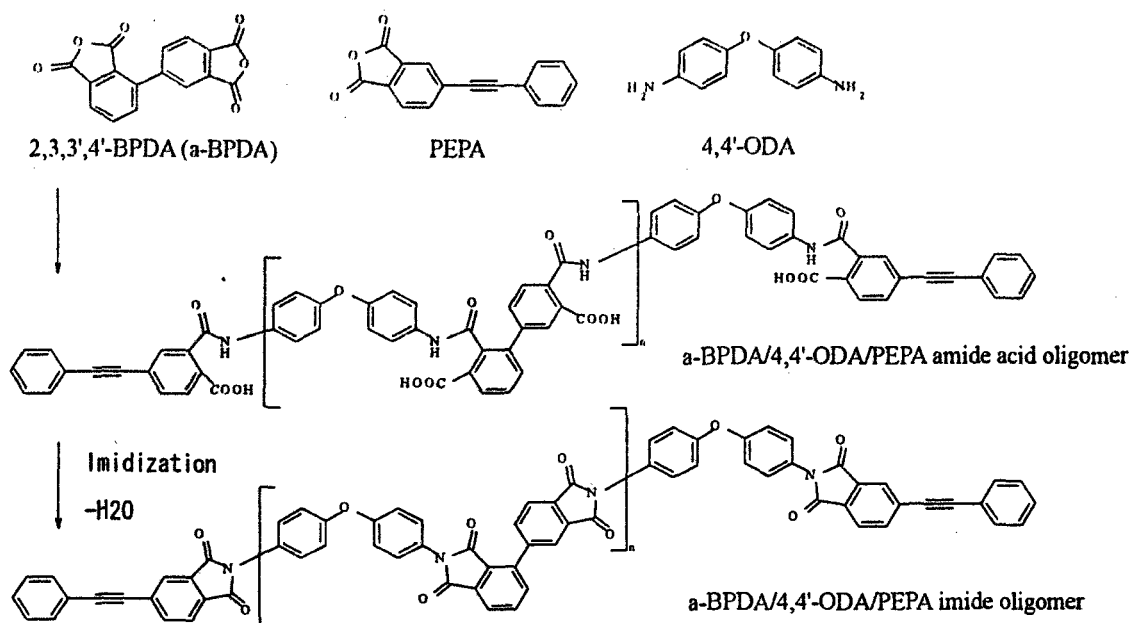


Fig. 1 Synthetic scheme of the imide oligomers from the reaction of a-BPDA, 4,4'-ODA, and PEPA

2.2 Processing of composites

2.2.1 Unidirectional composite

It is known that the lower molecular weight oligomer had the lower melting point and melt viscosity, when cured, the higher T_g, and lower fracture toughness, because of the higher crosslink density. In this study, the UD-composites with the ~1600 (n=2), and ~2500 g/mole (n=4) oligomers were fabricated, and mechanical properties were investigated. In this paper, the term TA-PI (1600), and TA-PI (2500) are used to describe the ~1600 and ~2500 g/mole version of the imide oligomers. The amide acid / NMP solutions were impregnated into T-800H carbon fiber (12K/bundle, Toray, Japan). The properties of the unidirectional prepreg tapes and imide oligomers are summarized in Table 2. Unidirectional (UD) composites were consolidated in an autoclave. In order to obtain a well-consolidated T800/Tri-A PI composite, the solvent (NMP) and reaction by-products (H₂O) should be removed before applying pressure. For the purpose, the prepreg was held at 250°C for 0.5 hr. Subsequently, pressure (0.3 MPa) was applied and the temperature was increased to 370°C and held for 1 hr.

Table 2 Unidirectional Prepreg and UD-Composite Properties

	n=2	n=4
Molecular weight (calc.), Mn	~1600	~2500
Prepreg solids (wt %)	36.4	30.4
Prepreg volatiles (wt %)	15.6	15.3
Carbon fiber	T800H 12K (445TEX)	
Carbon fiber areal weight (g/m ²)	240	
Prepreg areal weight (g/m ²)	365	350
Composite fiber fraction (vol. %)	64.2	69.6
Composite porosity (vol. %)	0.8	4.0

**Table 3 Plain Fabric Prepreg and Composite Properties
(Imide oligomer, n=4, Mn≈2500)**

<i>Cure temperature (°C) *</i>	360	370	380
Carbon fiber	T800H 12K (445TEX)		
Carbon cloth areal weight (g/m ²)	318		
Number of fiber bundles (/inch)	9 (for warp and fill)		
Prepreg solids (wt %)	36		
Prepreg volatiles (wt %)	14		
Prepreg areal weight (g/m ²)	432		
Composite architecture	0° /90° Plain woven fabric		
Composite fiber fraction (vol. %)	66.7	68.7	65.2
Composite resin contents (wt. %)	25.4	22.7	27.0
Composite porosity (vol. %)	1.7	3.3	1.7

* Cured for 1 hr under 5.5 MPa in a hot press.

2.2.2 Plain woven fabric composite

Plain fabric composites were also fabricated from prepreg route. The amide acid / NMP solutions were impregnated into Toray T-800 carbon fiber (12K/bundle) plain fabrics. The properties of the fabric prepreg are summarized in Table 3. Plain fabric composites were consolidated in a hot press. The solvent (NMP) and reaction by-products (H₂O) were removed at 250°C for 40 min, and pressure (5.5 MPa) was applied. The temperature was increased to 360, 370, and 380°C and held for 1 hr. The effect of cure temperature on the composite properties was also investigated.

3. RESULTS AND DISCUSSION

3.1 Rheological Properties of Imide Oligomers

The dynamic rheological behaviors of the imide oligomers are shown in Fig.2. The minimum viscosities were 3.4, 124, and 1750 Pa sec for the TA-PI (1600), TA-PI (2500), and TA-PI (5250), respectively, which corresponded to the viscosities reported for PETI-5 (5.0, 90, and 1000 Pa sec for Mw~1250, ~2500, and ~5000) [4]. It should be noticed that the melt viscosities above 310°C are not stable because of the phenylethynyl group reaction, and the melting point and melt viscosity below 310°C is more important for composite processability than the minimum viscosity. Therefore, lower molecular weight imide oligomers (<2500 g/mole) are suitable to improve processability.

3.2 Mechanical Properties

3.2.1 Unidirectional Composite

Fig.3 shows a DMA trace of the unidirectional T800/TA-PI composites. The storage (E'), loss (E'') moduli, and tanδ were plotted as a function of temperature. The estimated T_g determined from E' by setting up tangents to the linear portion of the curve before and after the modulus drop off was approximately 320°C and 290°C for the TA-PI (1600) and TA-PI (2500) composites, respectively. The decreases in storage modulus (E') above the glass transition temperature is relatively slight as compared to other kinds of polyimides.

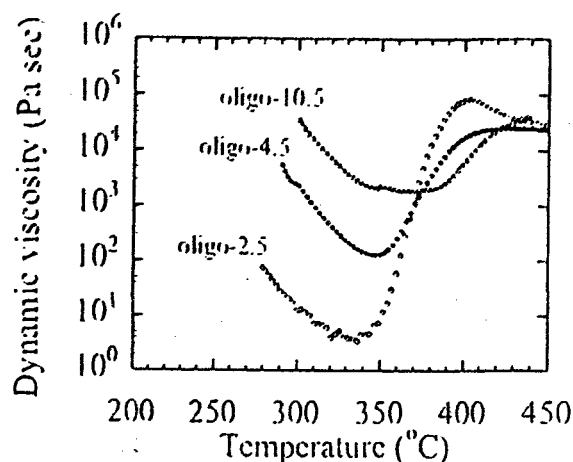


Fig. 2 Dynamic viscosity of the imide oligomers (n=2.5, 4.5, 10.5)

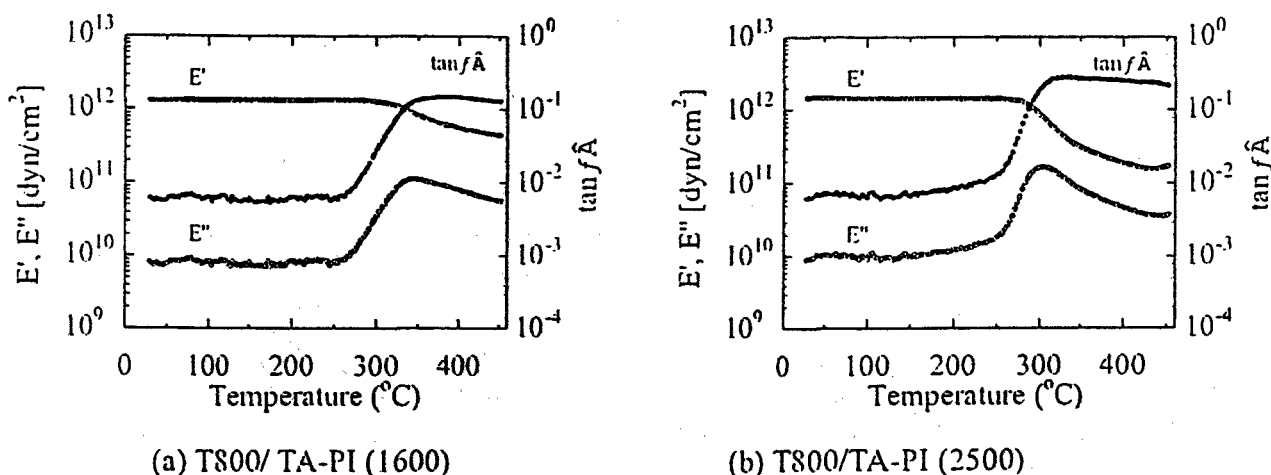


Fig. 3 Dynamic Mechanical Analysis (DMA) trace of the UD T800/TA-PI Composites.

Short beam shear strengths for the T800/TA-PI (1600) and T800/TA-PI (2500) composites are shown in Table 4. The literature data for the IM7/PETI-5 (5000) composites are cited in Table 4 [3]. Short beam shear tests were conducted on a servo-hydraulic testing machine (Model 8501, Instron, USA) under a constant displacement rate of 1.33 mm/min. Specimens were held for 1 min. after reaching the test temperature. The SBS strength of the TA-PI (1600) composite is superior as compared with the T800/TA-PI (2500) composite, which attributes to higher T_g as well as proper fiber volume fraction. Although thermoplastic deformation was slightly observed before interlaminar fracture at 300 °C, the apparent SBS strengths for the T800/TA-PI composites were quite excellent. The T800/TA-PI (1600) composite exhibits higher SBS strength at 177°C than the IM7/PETI-5 (5000) composite, which is due to higher T_g (~310 °C).

rate of 1.0 mm/min. Specimens were held for 20 minutes after reaching the test temperature with heating rate of 5 °C/min. The T800/TA-PI (2500) composite exhibits excellent tensile strengths, and degradation in tensile strength was not considerably observed up to 300°C. Flexural strengths of the TA-PI (1600) and TA-PI (2500) composites were determined at room temperature, and they were 2151 MPa, and 2194 MPa, respectively.

In spite of high crosslink density due to lower molecular weight, the T800/TA-PI composites exhibit excellent mechanical properties. It is supposed that the irregular and asymmetric structure as well as flexible endcapper (PEPA) contribute to the excellent mechanical properties such as fracture toughness, and elongation to failure.

Table 4 Mechanical Properties of UD-Composites

<i>Mechanical Properties</i>	<i>Temp.</i> (°C)	<i>T800H/TA-PI</i> (1600)	<i>T800H/TA-PI</i> (2500)	<i>IM7/PETI-5*</i>
Molecular weight (calc.), Mn		~1600	~2500	~5000
Composite fiber fraction (vol. %)		64.2	69.6	62
Composite porosity (vol. %)		0.8	4.0	1-2
SBS strength (MPa)	25	99.8	98.4	106.5
	177	75.9	56.9	62.8
	300	52.0**	41.9**	-
0° Tensile strength (MPa)	25	-	2672	2929
	177	-	2735	-
	250	-	2364	-
	300	-	2504	-
0° Flexural strength (MPa)	25	2151	2194	1788
	177	-	-	1442

* T.H. Hou, B. J. Jensen and P. M. Hergenrother, *J. Comp. Mater.*, 30 [1], 109-122 (1996).

** Thermoplastic deformation before interlaminar shear fracture

3.2.2 Plain woven fabric composite

Mechanical properties such as short beam shear (SBS) strength, tensile (NHT) strength, compressive (NHC) strength, and open hole compressive (OHC) strength were summarized in Table 5. It should be noticed that the SBS strengths are not actual interlaminar shear strength because of the improper fabric configuration (7 ply plain woven fabric). During the compressive tests for the composite cured at 360°C, local fracture at the loading edge of the specimen occurred before interlaminar fracture (*namely* brooming fracture), therefore the actual compressive strengths of the composite are supposed to be higher than the values shown in Table 5.

In spite of plain woven fabric, the composites exhibit excellent mechanical properties up to 300°C. The composite cured at 360°C has the most excellent mechanical properties. The composite cured at 360°C exhibits the least crosslink density, and the most flexible crosslink structure among the composites. It is supposed that the flexible crosslink structure contributes to good mechanical properties such as toughness and elongation, resulting in better compressive and tensile strengths.

Table 5 Mechanical Properties of Plain Fabric Composite

<i>Mechanical Properties</i>	<i>Temp.</i> (°C)	<i>T800H/TA-PI</i> (Mw2500)	<i>T800H/TA-PI</i> (Mw 2500)	<i>T800H/TA-PI</i> (Mw 2500)
Cure temperature (°C)		360	370	380
Composite fiber fraction (vol. %)		66.7	68.7	65.2
Composite porosity (vol. %)		1.7	3.3	1.7
SBS strength (MPa)	25	77.1	76.3	74.5
	177	55.3	51.6	51.2
	250	27.0*	25.7*	27.9*
	300	plastic	plastic	plastic
Tensile strength (MPa)	25	939	838	866
	177	988	843	849
	250	838	846	803
	300	784	788	771
Compressive strength (MPa)	25	545**	465	412
	177	435**	386	395
	250	386**	308	325
	300	301**	233	253
OHC strength (MPa)	25	289	287	288

* Thermoplastic deformation before interlaminar fracture

** Brooming fracture at the loading edge of the specimen

4. CONCLUSIONS

Preliminary studies for processing and mechanical properties of carbon fiber reinforced composites with the 1600 and 2600 g/mole version imide oligomers were conducted. The following conclusions were made:

1. Processing of the composites by routing prepreg consolidation was almost established.
2. In spite of higher crosslink density due to lower molecular weight (<2500 g/mole), the T800/TA-PI composites exhibit excellent mechanical properties at elevated temperature with high glass transition temperature.
3. It is supposed that the irregular and asymmetric structure derived from a-BPDA contribute to the excellent mechanical properties in addition to the flexible endcapper (PEPA).

Acknowledgement

The authors wish to sincerely thank Y. Asano, and A. Machii of Arisawa Manufacturing Co., Ltd. for the development of prepreg processing, and Dr. S. Bando, J. Gotoh of Kasawaki Heavy Industries, Ltd. for the development of composite processing.

5. REFERENCES

1. P. M. Hergenrother, and J. G. Smith, Jr, *Polymer*, 35(22), 4857 (1994)
2. J. W. Connell, J. G. Smith and P. M. Hergenrother, *Intl. SAMPE Tech. Conf. Series*, 30, 545 (1998)
3. T. H. Hou, B. J. Jensen and P. M. Hergenrother, *J. Comp. Mater.*, 30[1], 109-122 (1996)
4. J. G. Smith, Jr., J. W. Connell, and P. M. Hergenrother, *J. Comp. Mater.*, 34[7], 614-628 (2000)
5. P. M. Hergenrother, *SAMPE Journal*, 36 [1], 30-41 (2000)
6. M. Hasegawa, N. Sensui, S. Shindo and R. Yokota, *Macromolecules*, 32 p387 (1999)
7. R. Yokota, S. Yamamoto, S. Yano, T. Sawaguchi, M. Hasegawa, H. Yamaguchi, H. Ozawa, and R. Sato, *Proc. of 7th International Conference on Polyimides in Electronic Packing, The Society of Plastics Engineers, Oct. 16-18, (2000)*
8. R. Yokota, S. Yamamoto S. Yano, T. Sawaguchi, M. Hasegawa, H. Yamaguchi, H. Ozawa, and R. Sato, *High Performance Polymers*, 13, S61-S72 (2001)
9. R. Yokota, S. Yamamoto S. Yano, T. Sawaguchi, M. Hasegawa, H. Yamaguchi, H. Ozawa, and R. Sato, *Polyimides and Other High Temperature Polymers*, 1, 101-111 (2001)
10. T. Ogasawara, R. Yokota, Y. Shigenari, K. Miyagawa, H. Ozawa, M. Taguchi, and T. Ishikawa, *Proc. of 7th Japan International SAMPE Symposium and Exhibition (JISSE-7), Ed. By T. Ishikawa and S. Sugimoto, SAMPE, pp507-510 (2001)*